

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
20 February 2003 (20.02.2003)

PCT

(10) International Publication Number  
**WO 03/014134 A1**

(51) International Patent Classification<sup>7</sup>: **C07F 19/00**,  
7/00, 9/00, C23C 16/00

(21) International Application Number: PCT/GB02/03657

(22) International Filing Date: 7 August 2002 (07.08.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
0119224.4 7 August 2001 (07.08.2001) GB

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(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,  
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,  
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,  
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,  
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG,  
SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ,  
VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),  
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),  
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,  
ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK,  
TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,  
GW, ML, MR, NE, SN, TD, TG).

**Published:**

— with international search report

For two-letter codes and other abbreviations, refer to the "Guid-  
ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.

(54) Title: PRECURSORS FOR METALORGANIC CHEMICAL VAPOUR DEPOSITION

(57) Abstract: Metal compounds having a  $\beta$ -diketonate group containing an aryl group or a substituted derivative thereof as at least one ligand thereof and their use in chemical vapour deposition techniques.



**WO 03/014134 A1**

Title: Precursors for metalorganic chemical vapour deposition

### Description

This invention concerns precursors for metalorganic chemical vapour deposition (MOCVD). This invention is particularly, but not exclusively, concerned with precursors for growth of lead scandium tantalate  $\text{Pb}(\text{Sc}_{0.5}\text{Ta}_{0.5})\text{O}_3$  (PST) by MOCVD.

PST is a very sensitive pyroelectric material, which has several potential applications in uncooled thermal imaging, including military night vision, fire detection, medical diagnosis and automotive vision enhancement.

A variety of techniques can be used to grow thin films of PST, such as sputtering, sol-gel and MOCVD. Of these techniques MOCVD offers the most flexible approach having the potential for large area growth, excellent film uniformity and compositional control, high film densities and deposition rates and excellent step coverage at dimensions less than  $2\mu\text{m}$ . Furthermore, MOCVD processes are compatible with existing silicon chemical vapour deposition processes.

The application of PST films in pyroelectric devices has hitherto been restricted by the high temperature, typically above  $1000^\circ\text{C}$ , required to form the desired perovskite phase of the oxide and to eliminate the pyrochlore phase with its poor dielectric properties, which tends to form at relatively low substrate temperatures. Although PST in the perovskite phase has been grown at low temperatures by sol-gel techniques, there have been few reports of successful MOCVD studies. That is believed to be due to a lack of

suitable precursors with appropriate physical properties and decomposition characteristics, as well as incorrect choice of MOCVD technology.

Early MOCVD studies, F.W. Ainger et al, Prog. Cryst. Growth and Charact, 1991, 22 183, reported that a processing temperature of 800°C together with a post growth anneal were necessary to obtain the perovskite phase. More recent studies, Liu and Chen, Mater. Lett, 1996, 28,17, have demonstrated that PST in the correct perovskite phase can be grown in one step at substrate temperatures as low as 600°C. However, in both of those studies conventional MOCVD techniques were used, which involved passing a carrier gas through a precursor contained in a heated stainless steel container. Using that system, however, the precursors are susceptible to degradation over a period of time leading to compositional control problems in the layer being grown.

In order to overcome the problem of precursor degradation, liquid injection MOCVD has been used to deposit PST using a single solution of  $\text{Pb}(\text{thd})_2$ ,  $\text{Sc}(\text{thd})_3$  and  $\text{Ta}(\text{OEt})_5$  dissolved in tetrahydrofuran. (thd is 2,2,6,6-tetramethylheptane-3,5-dionate.) This technique maintains the precursor solution at room temperature until the point of use and minimises thermal degradation of the precursor.

Important requirements of the liquid injection MOCVD process are that co-precursors should, as far as possible, be compatible with similar physical properties (e.g. solubility, vapour pressure etc.) and should not undergo deleterious reactions with each other in solution. They should also evaporate at similar temperatures and deposit oxide films at similar substrate temperatures.

Although the precursor combination of  $\text{Pb}(\text{thd})_2$ ,  $\text{Sc}(\text{thd})_3$  and  $\text{Ta}(\text{OEt})_5$  allowed PST growth at low temperatures, these precursors are not compatible. For instance, problems were encountered due to the low volatility of the Sc precursor relative to the Pb and Ta precursors. Due to the low volatility of  $\text{Sc}(\text{thd})_3$ , a relatively high evaporator temperature, typically of 250-300°C is necessary to obtain adequate growth rates of scandium oxide,  $\text{Sc}_2\text{O}_3$ , and this can lead to thermal decomposition of the  $\text{Ta}(\text{OEt})_5$  source, causing blockages in the evaporator and injection system of the MOCVD apparatus and leading to PST films with poor uniformity.

A more thermally stable precursor is, therefore, required in order to improve the MOCVD process for the deposition of  $\text{Sc}_2\text{O}_3$  and  $\text{Pb}(\text{Sc}_{0.5}\text{Ta}_{0.5})\text{O}_3$ .

A tantalum oxide source which is more thermally stable than  $\text{Ta}(\text{OEt})_5$  would also be beneficial for the MOCVD of other complex oxides containing tantalum, such as strontium bismuth tantalate,  $\text{SrBi}_2\text{Ta}_2\text{O}_9$  (SBT) and strontium bismuth tantalate niobate,  $\text{SrBi}_2(\text{Ta}_x\text{Nb}_{1-x})_2\text{O}_9$  (SBTN), where it is desirable to use a tantalum precursor which deposits oxide in a similar temperature regime to the commonly used Sr and Bi precursors,  $\text{Sr}(\text{thd})_2$  and  $\text{Bi}(\text{thd})_3$ .

A more thermally stable Ta oxide precursor may also be desirable for the coating of glass substrates by CVD, such as on a float glass production line in which substrate temperatures in the order of 600°C are generally employed.

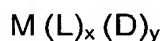
It has been surprisingly found that the dibenzoylmethanate group (1,3-diphenyl-1,3-propanedionate) can be used as a ligand to produce a tantalum oxide and other metal oxide precursors for deposition of metal oxides by chemical vapour deposition techniques.

According to a first aspect the present invention provides metal compounds having a  $\beta$ -diketonate group containing an aryl group or a substituted derivative thereof as at least one ligand thereof.

According to a second aspect the present invention provides a method of making metal compounds having a  $\beta$ -diketonate group or a substituted derivative thereof as at least one ligand comprising the steps of reacting a metal salt or a metal compound with a first ligand with the  $\beta$ -diketone or a salt thereof.

The present invention further provides a method of depositing metal oxides by MOCVD using metal compound precursors having a  $\beta$ -diketonate group containing an aryl group or a substituted derivative thereof as at least one ligand thereof.

Preferred precursors according to the invention have the following general formula:



wherein M is a metal selected from Ta, Pb, Ti, Ni, Cu, La, Nb, In and Zr,

L is a ligand, x is 0 or the valency of the metal minus y, D is a  $\beta$ -diketonate group of the following formula or a substituted derivative thereof



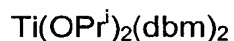
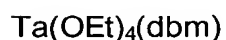
wherein  $R^1$  is an aryl group and  $R^2$  is an aryl group or an alkyl group

and y is 1 to 4.

The preferred ligand L is an alkoxy group having from 1 to 4 carbon atoms. Methoxy, ethoxy and isopropoxy groups are preferred ligands L.

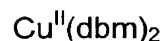
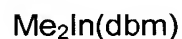
The preferred ligand D is a dibenzoylmethanate group (dbm). A preferred alternative might be benzoylacetate (1-phenyl-1,3-butanedionate).

Important precursors according to the invention include the following:



$\text{Pb}(\text{dbm})_2$  or  $\text{Pb}(\text{dbm})_2(\text{L}')$ , where  $\text{L}'$  is a unidentate or multidentate donor ligand

$\text{La}(\text{dbm})_3(\text{L}')$ , where  $\text{L}'$  is a unidentate or multidentate donor ligand



$\text{Cu}^{\text{I}}(\text{dbm})(\text{L})$  and  $\text{Cu}^{\text{I}}(\text{dbm})(\text{L})_2$ , wherein L is selected from alkene (e.g. trimethylvinyl silane, trimethoxy vinylsilane, triethoxyvinylsilane), alkyne, trialkyl phosphine (e.g.  $\text{PEt}_3$ ,  $\text{PMe}_3$  etc) and trialkyl phosphite, eg.  $\text{P}(\text{OEt})_3$ ,  $\text{P}(\text{OMe})_3$ .



$\text{Cu}^{\text{I}}(\text{bzac})(\text{L})$  and  $\text{Cu}^{\text{I}}(\text{bzac})(\text{L})_2$ , wherein L = trialkyl phosphite, eg.  $\text{P}(\text{OEt})_3$ ,  $\text{P}(\text{OMe})_3$ , trialkyl phosphine, eg.  $\text{PEt}_3$ ,  $\text{PMe}_3$  etc...) and bzac is benzoylacetate (1-phenyl-1,3-butanedionate)

It has been surprisingly found that precursors for chemical vapour deposition techniques that have dbm as a ligand have increased thermal

stability relative to precursors containing other  $\beta$ -diketonate ligands, such as thd and acetylacetonate (acac), which can lead to improved performance in certain liquid injection MOCVD applications, which may require the use of relatively high evaporator or substrate temperatures.

The aryl group or groups of the ligand D, such as dbm, may be substituted and it is envisaged that different substituents may alter the thermal stability and/or volatility of the resultant precursor possibly due to the electron attracting or donating property of the substituents. Thus, it is envisaged that, where previously a precursor for a particular metal oxide that was a good match for codeposition with other precursors was not available, a suitable precursor could be produced having, for example, dbm or a suitably substituted dbm as a ligand. Examples of suitable substituents for the aryl groups of the ligand D will include electron donating groups, such as  $\text{NH}_2$ ,  $\text{NR}_3$ ,  $\text{PR}_3$ ,  $\text{OR}$  and  $\text{R}$ , wherein  $\text{R}$  = alkyl, and electron withdrawing groups, such as  $\text{NO}_2$ ,  $\text{CN}$ , halide and  $\text{SO}_3\text{H}$ . One or two substituents may be provided on an aryl group.

Precursors according to the invention may be used in depositing single or mixed oxide layers or metal films. Examples of uses of precursors of the invention include the following:

$\text{Pb}(\text{dbm})_2$  and its adducts with donor ligands, such as crown ethers, may be used with scandium and tantalum precursors for deposition of  $\text{Pb}(\text{Sc}_{0.5}\text{Ta}_{0.5})\text{O}_3$  and with zirconium and titanium precursors for deposition of  $\text{Pb}(\text{Zr,Ti})\text{O}_3$ .

$\text{La}(\text{dbm})_3(\text{L})$  may be used with a manganese precursor for deposition of  $\text{LaMnO}_3$  and with a nickel precursor for deposition of  $\text{LaNiO}_3$ .

$\text{Ni}(\text{dbm})_2$  may be used as a precursor for deposition of  $\text{LaNiO}_3$ .

$\text{Ti}(\text{OPr}^i)_2(\text{dbm})_2$  may be used in the deposition of  $\text{TiO}_2$ ,  $(\text{Ba}, \text{Sr}) \text{TiO}_3$  (BST) and  $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$  (PZT).

$\text{Cu}^{\text{II}}(\text{dbm})_2$  and  $\text{Cu}^{\text{I}}(\text{dbm})(\text{L})$  may be used as precursors for depositing copper oxide or copper films by chemical vapour deposition.

$\text{Me}_2\text{In}(\text{dbm})$  may be used as a precursor for depositing indium oxide layers alone or with tin.

$\text{Ta}(\text{OEt})_4(\text{dbm})$  has potential applications as a precursor for  $\text{Pb}(\text{Sc}_{0.5}, \text{Ta}_{0.5})\text{O}_3$  and for chemical vapour deposition of  $\text{SrBi}_2\text{Ta}_2\text{O}_9$  and  $\text{Ta}_2\text{O}_5$ .

$\text{Nb}(\text{OEt})_4(\text{dbm})$  has potential applications for the MOCVD of  $\text{Pb}(\text{Mg}_{0.33}\text{Nb}_{0.33})\text{O}_3$ ,  $\text{SrBi}_2(\text{Ta}_x\text{Nb}_{1-x})_2\text{O}_9$  and niobium oxide.

$\text{Zr}(\text{dbm})_4$  has applications in  $\text{ZrO}_2$  CVD at high substrate temperatures.

This invention will be further described with reference to the accompanying drawings, in which:

Figure 1 shows an envisaged structure for  $\text{Ta}(\text{OEt})_4(\text{dbm})$ ;

Figure 2 shows an envisaged structure for  $\text{Nb}(\text{OEt})_4(\text{dbm})$ ;

Figure 3 shows an envisaged structure for lead bis-(dbm);

Figure 4 is a graph showing the variation of the growth rate of tantalum oxide with substrate temperature for  $\text{Ta}(\text{OEt})_4(\text{dbm})$  on silicon substrate;

Figure 5 is a graph showing the variation of tantalum oxide growth rate with evaporator temperature for  $\text{Ta}(\text{OEt})_4(\text{dbm})$  on silicon substrate;

Figure 6 is a graph showing the variation of niobiumoxide growth rate with substrate temperature for  $\text{Nb}(\text{OEt})_4(\text{dbm})$ ; and



Figure 7 is a graph showing variation of niobium oxide growth rate with evaporator temperature for Nb(OEt)<sub>4</sub>(dbm).

This invention will now be further described by means of the following examples.

### Example 1

#### Preparation of Ta(OEt)<sub>4</sub>(dbm)

To a stirred solution of Ta(OEt)<sub>5</sub> (5.48g, 13.5mmol) in approximately 20cm<sup>3</sup> of toluene was added one equivalent of Hdbm (3.03g, 13.5mmol). The resulting mixture was then refluxed for 2 hours and all the volatiles were removed *in vacuo* to give a yellow solid. This was re-dissolved in the minimum quantity of hot toluene and left overnight at 4°C to yield yellow crystals of Ta(OEt)<sub>4</sub>(dbm). Yield: 6.47g, 84.9%.

Anal. Calc. for C<sub>23</sub>H<sub>31</sub>O<sub>6</sub>Ta: C, 47.3; H, 5.4. Found: C, 47.0; H, 5.4%. m.p. 65-67°C.

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 30°C): δ 1.04 [6H, t, OCH<sub>2</sub>CH<sub>3</sub>]; <sup>3</sup>J<sub>HH</sub> = 6.9Hz, 1.38 [6H, t, OCH<sub>2</sub>CH<sub>3</sub>]; <sup>3</sup>J<sub>HH</sub> = 6.9Hz, 4.28 [4H, q, OCH<sub>2</sub>CH<sub>3</sub>]; <sup>3</sup>J<sub>HH</sub> = 6.9Hz, 4.83 [4H, q, OCH<sub>2</sub>CH<sub>3</sub>]; <sup>3</sup>J<sub>HH</sub> = 6.9Hz, 6.90 [1H, s, C<sub>6</sub>H<sub>5</sub>COCHCOC<sub>6</sub>H<sub>5</sub>], 7.23 [6H, m, C<sub>6</sub>H<sub>5</sub>COCHCOC<sub>6</sub>H<sub>5</sub>], 8.05 [4H, m, C<sub>6</sub>H<sub>5</sub>COCHCOC<sub>6</sub>H<sub>5</sub>].

<sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 30°C): δ 19.3 [OCH<sub>2</sub>CH<sub>3</sub>], 19.8 [OCH<sub>2</sub>CH<sub>3</sub>], 66.2 [OCH<sub>2</sub>CH<sub>3</sub>], 69.6 [OCH<sub>2</sub>CH<sub>3</sub>], 96.1 [C<sub>6</sub>H<sub>5</sub>COCHCOC<sub>6</sub>H<sub>5</sub>], 128.0, [C<sub>6</sub>H<sub>5</sub>COCHCOC<sub>6</sub>H<sub>5</sub>], 129.4 [C<sub>6</sub>H<sub>5</sub>COCHCOC<sub>6</sub>H<sub>5</sub>], 133.0 [C<sub>6</sub>H<sub>5</sub>COCHCOC<sub>6</sub>H<sub>5</sub>], 138.3 [C<sub>6</sub>H<sub>5</sub>COCHCOC<sub>6</sub>H<sub>5</sub>], 184.2 [C<sub>6</sub>H<sub>5</sub>COCHCOC<sub>6</sub>H<sub>5</sub>].

IR (Nujol, cm<sup>-1</sup>) 1598m, 1526s, 1319m, 1236w, 1130w, 1110m, 1069s, 980w, 916m, 721m, 668m.

Figure 1 of the drawings shows the envisaged structure of Ta(OEt)<sub>4</sub>(dbm).

### Example 2

#### Preparation of Nb(OEt)<sub>4</sub>(dbm)

Nb(OEt)<sub>4</sub>(dbm) was prepared using identical methodology to Ta(OEt)<sub>4</sub>(dbm). Reaction of Nb(OEt)<sub>5</sub> (4.66g, 12.2mmol) with one equivalent of Hdbm (2.74g, 12.2mol) in toluene gave yellow crystals. Yield: 4.56g, 75.4%.

Anal. Calc. for C<sub>23</sub>H<sub>31</sub>O<sub>6</sub>Nb: C, 55.7; H, 6.3. Found: C, 54.6; H, 6.2%. m.p. 72-74°C.

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 30°C):  $\delta$  1.18 [6H, t, OCH<sub>2</sub>CH<sub>3</sub>]; <sup>3</sup>J<sub>HH</sub> = 6.9Hz, 1.54 [6H, t, OCH<sub>2</sub>CH<sub>3</sub>]; <sup>3</sup>J<sub>HH</sub> = 7.0Hz, 4.35 [4H, q, OCH<sub>2</sub>CH<sub>3</sub>]; <sup>3</sup>J<sub>HH</sub> = 6.9Hz, 4.91 [4H, q, OCH<sub>2</sub>CH<sub>3</sub>]; <sup>3</sup>J<sub>HH</sub> = 7.0Hz, 7.03 [1H, s, C<sub>6</sub>H<sub>5</sub>COCHCOC<sub>6</sub>H<sub>5</sub>], 7.35 [6H, m, C<sub>6</sub>H<sub>5</sub>COCHCOC<sub>6</sub>H<sub>5</sub>], 8.19 [4H, m, C<sub>6</sub>H<sub>5</sub>COCHCOC<sub>6</sub>H<sub>5</sub>].

<sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 30°C):  $\delta$  18.9 [OCH<sub>2</sub>CH<sub>3</sub>], 19.4 [OCH<sub>2</sub>CH<sub>3</sub>], 67.7 [OCH<sub>2</sub>CH<sub>3</sub>], 71.7 [OCH<sub>2</sub>CH<sub>3</sub>], 95.0 [C<sub>6</sub>H<sub>5</sub>COCHCOC<sub>6</sub>H<sub>5</sub>], 128.0, [C<sub>6</sub>H<sub>5</sub>COCHCOC<sub>6</sub>H<sub>5</sub>], 129.3 [C<sub>6</sub>H<sub>5</sub>COCHCOC<sub>6</sub>H<sub>5</sub>], 132.7 [C<sub>6</sub>H<sub>5</sub>COCHCOC<sub>6</sub>H<sub>5</sub>], 138.8 [C<sub>6</sub>H<sub>5</sub>COCHCOC<sub>6</sub>H<sub>5</sub>], 183.9 [C<sub>6</sub>H<sub>5</sub>COCHCOC<sub>6</sub>H<sub>5</sub>].

IR (Nujol, cm<sup>-1</sup>) 1597s, 1530vs, 1480s, 1453s, 1365vs, 1313s, 1278w, 1238m, 1183w, 1134m, 1101vs, 1063vs, 1026s, 943w, 913vs, 790w, 776w, 723m, 700w, 690m, 620s.

Table 1 below shows H NMR Data ( $\delta$ ) recorded in C<sub>6</sub>D<sub>6</sub>.

Table 1

	OR		Dbm	
Compound	OCH <sub>2</sub>	CH <sub>3</sub>	PhCOCHCOPh	C <sub>6</sub> H <sub>5</sub> COCHCOC <sub>6</sub> H <sub>5</sub>
Ta(OEt) <sub>4</sub> (dbm)	4.28 (q); <sup>3</sup> J <sub>HH</sub> = 6.9Hz	1.04 (t); <sup>3</sup> J <sub>HH</sub> = 6.9Hz	6.90 (s)	7.23 (m)
	4.83 (q); <sup>3</sup> J <sub>HH</sub> = 6.9Hz	1.38 (t); <sup>3</sup> J <sub>HH</sub> = 6.9Hz		8.05 (m)
Nb(OEt) <sub>4</sub> (dbm)	4.35 (q); <sup>3</sup> J <sub>HH</sub> = 6.9Hz	1.18 (t); <sup>3</sup> J <sub>HH</sub> = 6.9Hz	7.03 (s)	7.35 (m)
	4.91 (q); <sup>3</sup> J <sub>HH</sub> = 7.0Hz	1.54 (t); <sup>3</sup> J <sub>HH</sub> = 7.0Hz		8.19 (m)

Table 2 below shows <sup>13</sup>C{<sup>1</sup>H} NMR Data (δ) recorded in C<sub>6</sub>D<sub>6</sub>.

Table 2

	OR		Dbm		
Compound	OCH <sub>2</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> COCHCOC <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> COCHCOC <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> COCHCOC <sub>6</sub> H <sub>5</sub>
Ta(OEt) <sub>4</sub> (dbm)	66.2	19.3	96.1	128.0	184.2
	69.6	19.8		129.4	
				133.0	
				138.3	
Nb(OEt) <sub>4</sub> (dbm)	67.7	18.9	95.0	128.0	183.9
	71.7	19.4		129.3	
				132.7	
				138.8	

Peak at 128.0 cannot be positively identified due to C<sub>6</sub>D<sub>6</sub> signal obscuring the area. <sup>13</sup>C peaks assigned from Atlas of Carbon-13 NMR Data.

Figure 2 of the drawings shows the envisaged structure for Nb(OEt)<sub>4</sub>(dbm).

### Example 3

Procedure and characterisation for lead bis-(dbm)

1. 0.5 g of NaOH in 15ml of methanol added to 2.80g of dibenzoylmethane (Hdbm) in 30ml of warm methanol.
2. 2.37 g of lead acetate dissolved in 20ml warm methanol and added to Na (dbm) solution initially forming a clear yellow solution and suddenly a bright yellow ppt.
3. Precipitate added to about 10ml of H<sub>2</sub>O. The solution was then filtered and washed with water and methanol.
4. Recrystallised from hot ethyl acetate and left at room temperature for 1 week

Yield - 3.82g (93 %) M.Pt - ~220°C (with decomposition)

C/H Analysis for PbC<sub>30</sub>H<sub>22</sub>O<sub>4</sub> is shown in Table 3 below.

Table 3

C/H Analysis	Calculated	Experimental
Carbon	55.12	54.35
Hydrogen	3.39	3.28

XRD supplied

The envisaged structure for lead bis-(dbm) is shown in Figure 3 of the accompanying drawings.

#### Example 4

Procedure and Characterisation for Titanium bis-isopropoxide bis-(dibenzoylmethanate)

1. Schlenck charged with 30ml of toluene and 4.54g of DBM added.
2. 3ml of Ti(OPr<sup>i</sup>)<sub>4</sub> added resulting in clear orange solution. Sudden ppt formed after a few minutes.

3. Refluxed for 1 hour and solvent removed *in vacuo* resulting in a bright orange/yellow solid. Recrystallised from small amount of toluene at 4°C.

Yield 4.89g (79%)

C/H Analysis for  $\text{TaC}_{36}\text{H}_{36}\text{O}_6$  : (calculated) C% 70.59, H% 5.83;  
(experimental) C%70.86, H% 6.11

H NMR ( $\text{C}_6\text{D}_6$  at 30°C)  $\delta$  1.46 (12H, d,  $(\text{CH}_3)_2\text{CH}$ ),  $\delta$  5.35 (2H, m,  $(\text{CH}_3)_2\text{CH}$ ),

$\delta$  7.04 (2H, s,  $\text{PhC}(\text{O})\text{CHC}(\text{O})\text{Ph}$  + 8H, m, (meta or ortho position on phenyl rings)

$\delta$  7.3 (4H, m, para position on phenyl rings),  $\delta$  7.98 and 8.31 (8H (collectively), m, (meta or ortho position on phenyl rings)

#### Example 5

Tantalum oxide deposition from  $\text{Ta}(\text{OEt})_4$  (dbm)

The conditions used were those below

Solution strength in heptane 0.05M

Injection rate of 8 ml/hour

Deposition for one hour

Two substrates were placed on the susceptor. The first being always a silicon one towards the front of the susceptor and the second a sapphire one towards the rear of the susceptor. In all cases the deposition on the sapphire was thicker.

The results are shown below in tables 4, 5 and 6 below. One additional run was carried out at higher pressure 200mbar which gave very little deposition at all.

Table 4

Substrate Temp °C	Substrate Thickness nm	Substrate Thickness Nm
400	91	167
450	202	374
500	363	
550	689	1102
600	727	1097
650	861	1283

Comments on growth conditions:

Growth pressure 20mbar

N<sub>2</sub> flow 400 cc/min

O<sub>2</sub> flow 100 cc/min

0.05M solution in heptane

Injection rate 8 ml/hr

1 hour growth

Evaporator temp 225°C

Table 5

Evaporator Temp °C	Si thickness nm	Al <sub>2</sub> O <sub>3</sub> thickness nm
150	471	558
175	825	1045
200	820	1156
225	727	1097
275	656	905

Comments on growth conditions:

Substrate temperature 600°C

N<sub>2</sub> flow 400cc/min

O<sub>2</sub> flow 100cc/min

Growth pressure 20mbar

Table 6

O <sub>2</sub> flow cc/min	Si thickness Nm	Al <sub>2</sub> O <sub>3</sub> thickness nm
0	876	1057
100	820	1156
200	816	974

Comments on growth conditions:

Substrate temp 600°C

Evaporator 200°C

Growth pressure 20mbar

Example 6

Niobium oxide deposition from Nb(OEt)<sub>4</sub>(dbm)

The conditions used were as follows

Nb(OEt)<sub>4</sub>(dbm) solution concentration: 0.08M in a mixed heptane /THFsolvent

Carrier gas flow 400 cc/min nitrogen

Oxygen flow 100cc/min

Reactor pressure 20 mbar

Injection rate 5ml/hour

Amount of solution injected 6.25 ml

The results are a thickness obtained for the injection of a fixed volume of precursor. Two silicon substrates were used. The thickness data listed below in Table 7 is taken from the substrate placed towards the front of the susceptor.

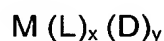
Table 7

Run number	Dep.Temp. (C)	Thickness (nm)	Vaporiser temp (C)
961	500	868	200
962	400	175	200
963	600	1240	200
965	450	456	200
966	600	1080	225
967	600	856	175



Claims:

1. Metal compounds having a  $\beta$ -diketonate group containing an aryl group or a substituted derivative thereof as at least one ligand thereof.
2. A metal compound as claimed in claim 1 having the following general formula:



wherein M is a metal selected from Ta, Pb, Ti, Ni, Cu, La, Nb, In and Zr,

L is a ligand, x is 0 or the valency of the metal minus y, D is a  $\beta$ -diketonate group of the following formula or a substituted derivative thereof



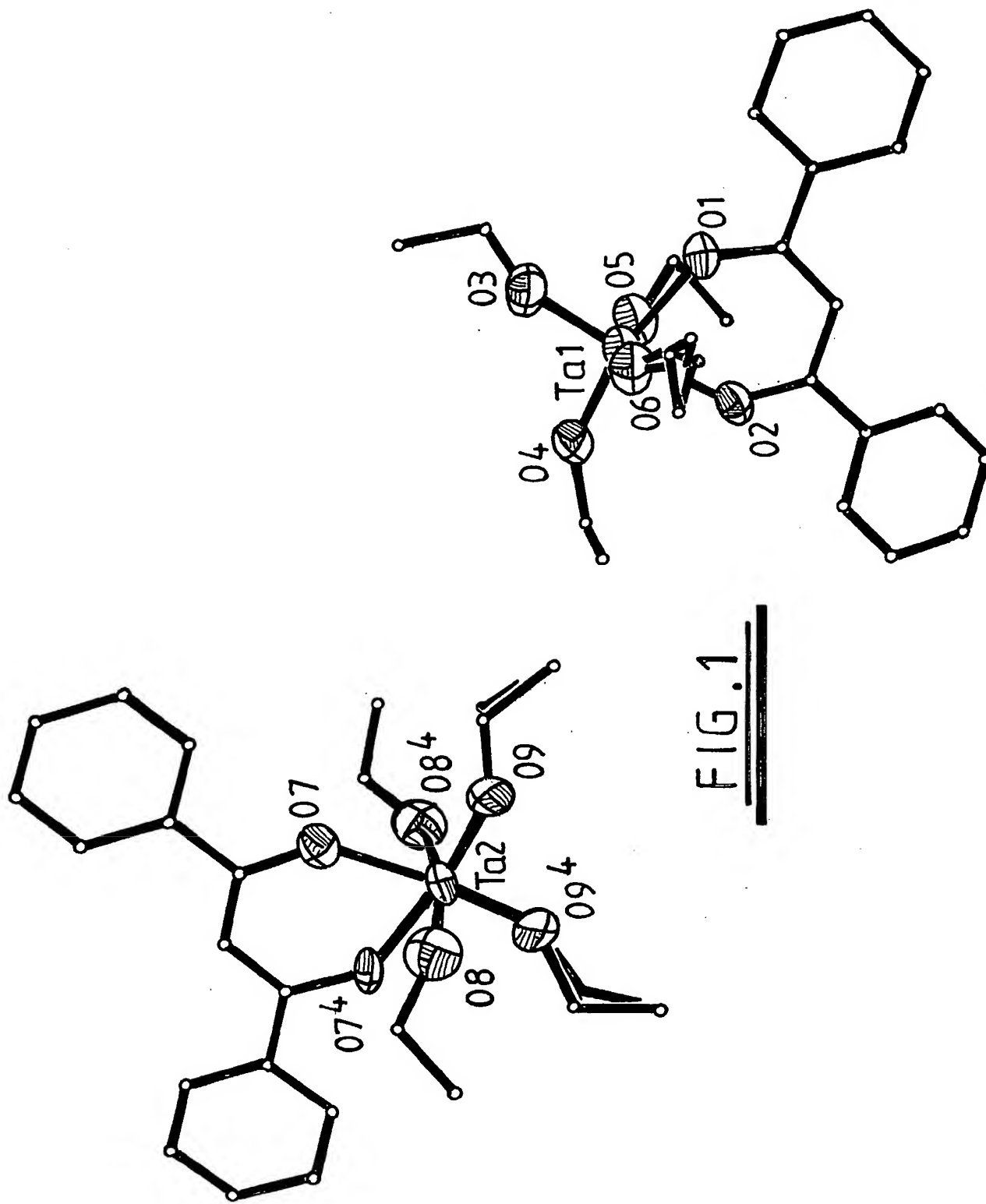
wherein  $R^1$  is an aryl group and  $R^2$  is an aryl group or an alkyl group and y is 1 to 4.

3. A metal compound as claimed in claim 2, wherein the ligand L is an alkoxy group having from 1 to 4 carbon atoms.
4. A metal compound as claimed in claim 3, wherein the ligand L is a methoxy, ethoxy or isopropoxy group.
5. A metal compound as claimed in claim 2, 3 or 4, wherein the ligand D is a dibenzoylmethanate group (dbm).
6. A metal compound as claimed in claim 2, 3 or 4, wherein the ligand D is benzoylacetate (1-phenyl-1,3-butanedionate).
7.  $Ta(OEt)_4(dbm)$ .
8.  $Ti(OPr^i)_2(dbm)_2$ .

9.  $\text{Pb}(\text{dbm})_2$  or  $\text{Pb}(\text{dbm})_2(\text{L}')$ , where  $\text{L}'$  is a unidentate or multidentate donor ligand.
10.  $\text{La}(\text{dbm})_3(\text{L}')$ , where  $\text{L}'$  is a unidentate or multidentate donor ligand.
11.  $\text{Ni}(\text{dbm})_2$ .
12.  $\text{Me}_2\text{In}(\text{dbm})$ .
13.  $\text{Cu}^{\text{II}}(\text{dbm})_2$ .
14.  $\text{Nb}(\text{OEt})_4\text{dbm}$ .
15.  $\text{Cu}^{\text{I}}(\text{dbm})(\text{L})$ , wherein  $\text{L}$  is selected from alkene, alkyne and trialkyl phosphine.
16. A compound as claimed in claim 15, wherein the alkene is selected from trimethylvinyl silane, trimethoxy vinylsilane and triethoxyvinylsilane.
17. A compound as claimed in claim 15, wherein the trialkyl phosphine is triethyl phosphine.
18.  $\text{Zr}(\text{dbm})_4$ .
19.  $\text{Cu}^{\text{I}}(\text{dbm})(\text{L})$  and  $\text{Cu}^{\text{I}}(\text{dbm})(\text{L})_2$ , wherein  $\text{L}$  = trialkyl phosphite or trialkyl phosphine.
20. A compound as claimed in claim 21, wherein the trialkyl phosphite is selected from  $\text{P}(\text{OEt})_3$  and  $\text{P}(\text{OMe})_3$ .
21. A compound as claimed in claim 19, wherein the trialkyl phosphine is selected from  $\text{PEt}_3$  and  $\text{PMe}_3$ .
22.  $\text{Cu}^{\text{I}}(\text{bzac})(\text{L})$  and  $\text{Cu}^{\text{I}}(\text{bzac})(\text{L})_2$ , wherein  $\text{L}$  = trialkyl phosphite or trialkyl phosphine and bzac is benzoylacetate (1-phenyl-1,3-butanedionate).
23. A compound as claimed in claim 22, wherein the trialkyl phosphite is selected from  $\text{P}(\text{OEt})_3$  and  $\text{P}(\text{OMe})_3$ .

24. A compound as claimed in claim 22, wherein the trialkyl phosphine is selected from  $\text{PEt}_3$  and  $\text{PMe}_3$ .
25. Compounds as claimed in any one of claims 1 to 6, wherein the aryl groups have one or two substituent groups thereon.
26. Compounds as claimed in claim 25, wherein the aryl groups of the have substituents selected from electron donating groups
27. Compounds as claimed in claim 26, wherein the electron donating groups are selected from  $\text{NH}_2$ ,  $\text{NR}_3$ ,  $\text{PR}_3$ , OR and R, wherein R = alkyl.
28. Compounds as claimed in claim 25, wherein the aryl groups of the have substituents selected from electron withdrawing groups.
29. Compounds as claimed in claimed in claim 28, wherein the electron withdrawing groups are selected from  $\text{NO}_2$ , CN, halide and  $\text{SO}_3\text{H}$ .
30. A method of making metal compounds having a  $\beta$ -diketonate group or a substituted derivative thereof as at least one ligand comprising the steps of reacting a metal salt or a metal compound with a first ligand with the  $\beta$ -diketone or a salt thereof.
31. A method of depositing metal oxides by MOCVD using metal compound precursors as claimed in any one of claims 1 to 29.
32. A method as claimed in claim 31, wherein  $\text{Pb}(\text{dbm})_2$  and its adducts with donor ligands, such as crown ethers, are used with scandium and tantalum precursors for deposition of  $\text{Pb}(\text{Sc}_{0.5}\text{Ta}_{0.5})\text{O}_3$  or with zirconium and titanium precursors for deposition of  $\text{Pb}(\text{Zr,Ti})\text{O}_3$ .
33. A method as claimed in claim 31, wherein  $\text{La}(\text{dbm})_3(\text{L})$  is used with a manganese precursor for deposition of  $\text{LaMnO}_3$  or with a nickel precursor for deposition of  $\text{LaNiO}_3$ .

34. A method as claimed in claim 31, wherein  $\text{Ni}(\text{dbm})_2$  is used as a precursor for deposition of  $\text{LaNiO}_3$ .
35. A method as claimed in claim 31, wherein  $\text{Ti}(\text{OPr}^j)_2(\text{dbm})_2$  is used in the deposition of  $\text{TiO}_2$ ,  $(\text{Ba}, \text{Sr}) \text{TiO}_3$  (BST) or  $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$  (PZT).
36. A method as claimed in claim 31, wherein  $\text{Cu}^{\text{II}}(\text{dbm})_2$  or  $\text{Cu}^{\text{I}}(\text{dbm})(\text{L})$  is used as a precursor for depositing copper oxide or copper films.
37. A method as claimed in claim 31, wherein  $\text{Me}_2\text{In}(\text{dbm})$  is used as a precursor for depositing indium oxide layers alone or with tin.
38. A method as claimed in claim 31, wherein  $\text{Ta}(\text{OEt})_4(\text{dbm})$  is used as a precursor for deposition of  $\text{Pb}(\text{Sc}_{0.5}, \text{Ta}_{0.5})\text{O}_3$  or for deposition of  $\text{SrBi}_2\text{Ta}_2\text{O}_9$  or  $\text{Ta}_2\text{O}_5$ .
39. A method as claimed in claim 31, wherein  $\text{Nb}(\text{OEt})_4(\text{dbm})$  is used as a precursor MOCVD of  $\text{Pb}(\text{Mg}_{0.33}\text{Nb}_{0.33})\text{O}_3$ ,  $\text{SrBi}_2(\text{Ta}_x\text{Nb}_{1-x})_2\text{O}_9$  or niobium oxide.
40. A method as claimed in claim 31, wherein  $\text{Zr}(\text{dbm})_4$  is used as a precursor for deposition of  $\text{ZrO}_2$  at high substrate temperatures.



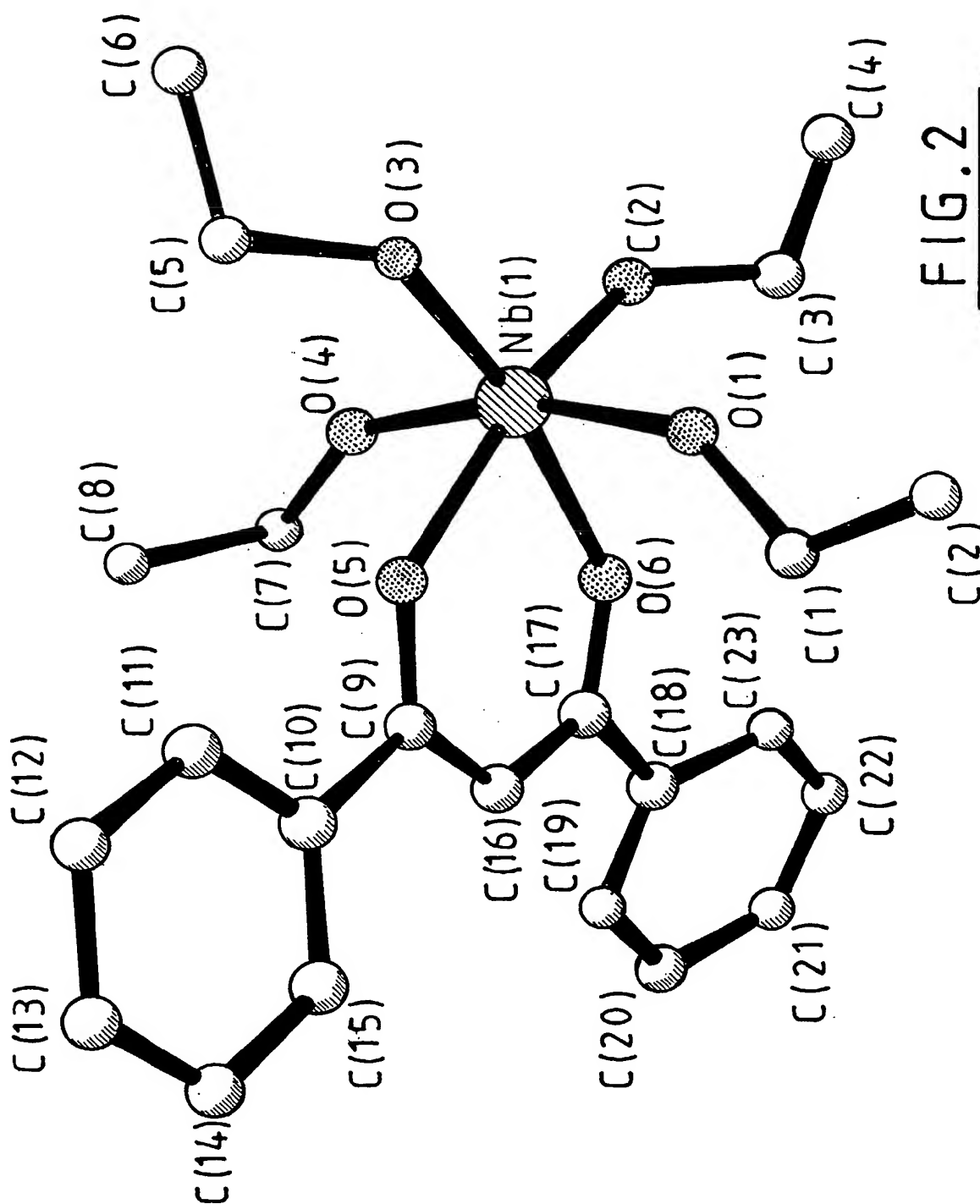
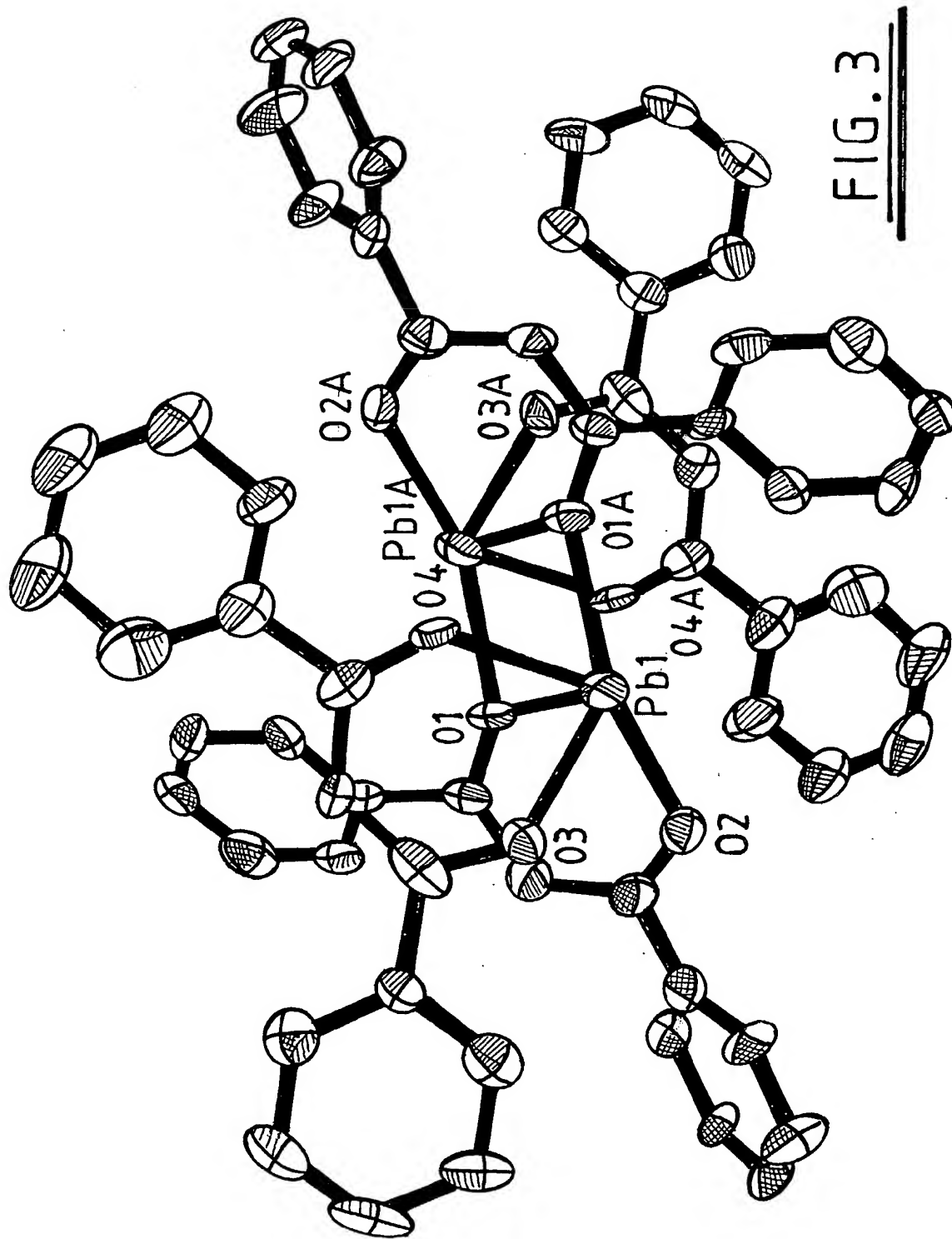
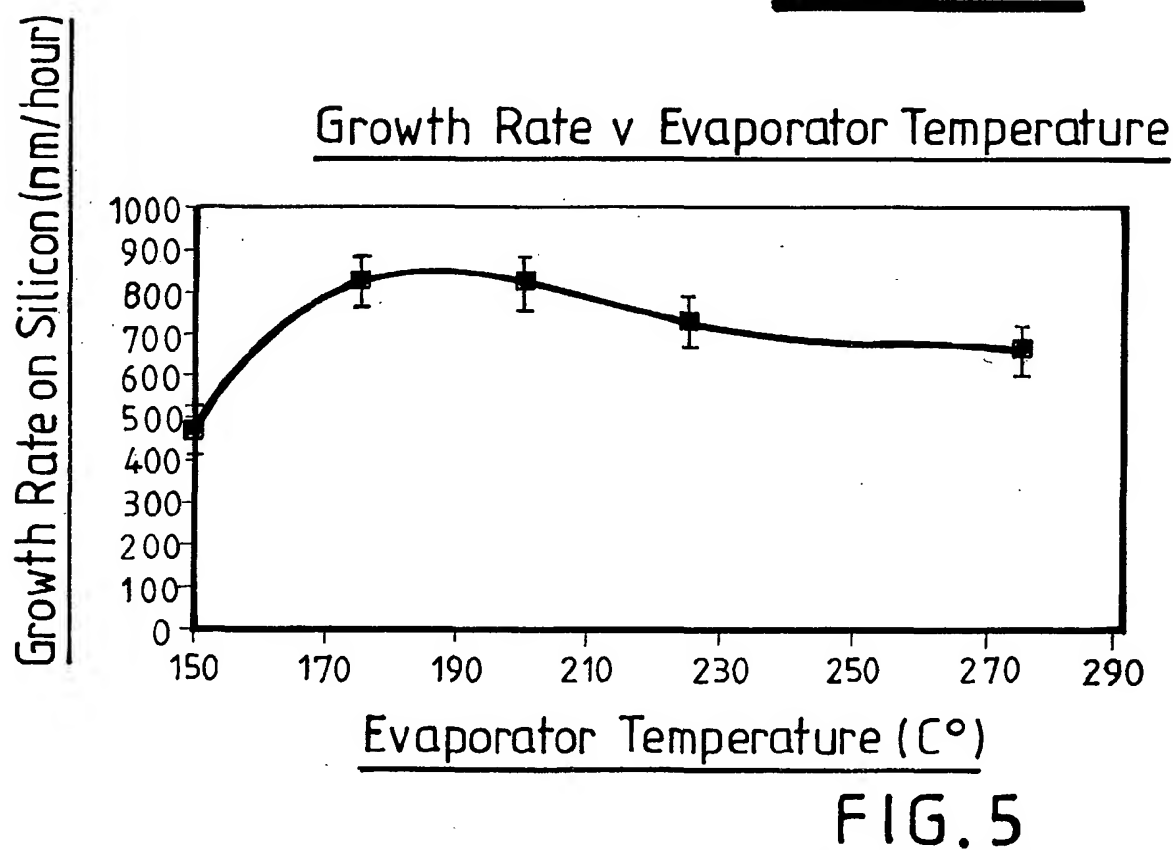
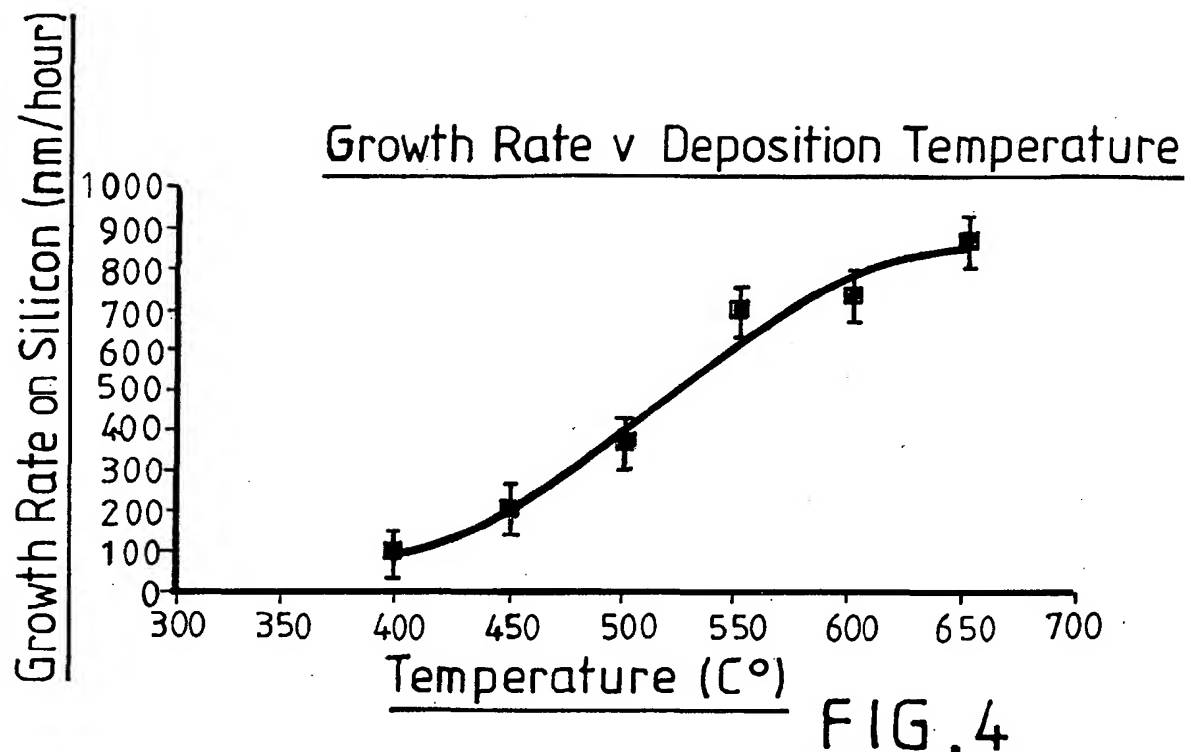
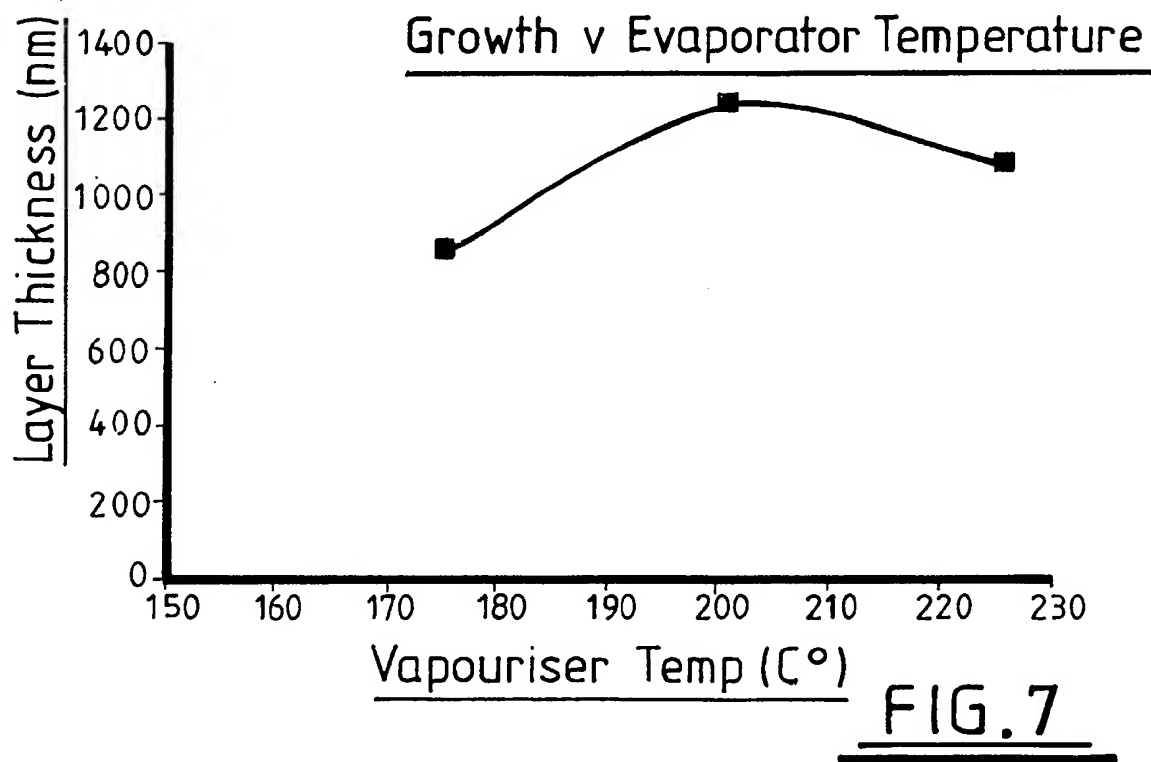
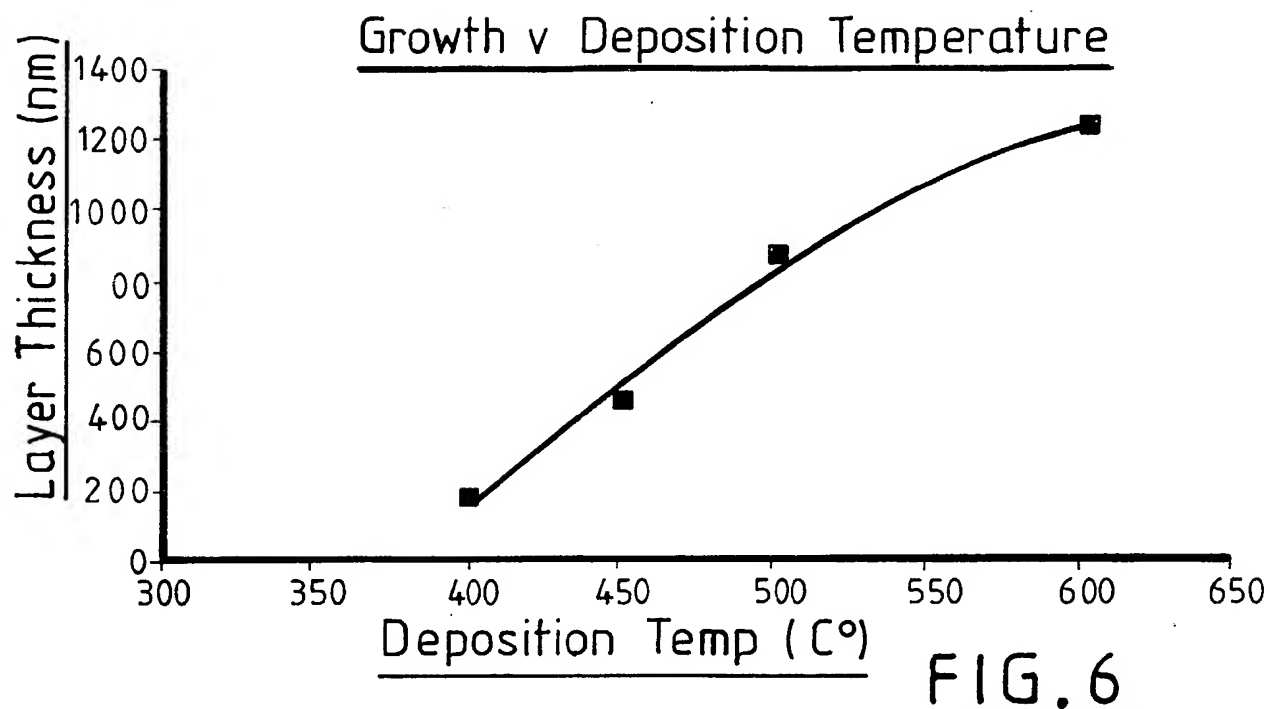


FIG. 2









# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 02/03657

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07F19/00 C07F7/00 C07F9/00 C23C16/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07F C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 153 000 A (TAKIMOTO, H.H. ET AL.) 13 October 1964 (1964-10-13) example 1 ---	1-5, 8
X	WO 84 03042 A (BYK GULDEN LOMBERG CHEMISCHE FABRIK GMBH) 16 August 1984 (1984-08-16) examples 1-13 ---	1-6
X	KAPOOR, R. N. ET AL: "Organic compounds of niobium and tantalum. Reactions of niobium and tantalum pentaethoxides with dibenzoylmethane" BULL. CHEM. SOC. JPN. (1967), 40(6), 1384-6 , 1967, XP002219905 the whole document --- --/--	1-7, 11, 14



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

\* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \* & \* document member of the same patent family

Date of the actual completion of the international search

14 November 2002

Date of mailing of the international search report

21/11/2002

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## INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 02/03657

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE CA 'Online!  CHEMICAL ABSTRACTS SERVICE, COLUMBUS,  OHIO, US;  STARY, J. ET AL: "Systematic study of the  solvent extraction of  metal.beta.-diketonates"  retrieved from STN  Database accession no. 58:76615  XP002219906  abstract  &amp; ANAL. CHIM. ACTA (1963), 28, 227-35,</p> <p>---</p>	1-6,9
X	<p>DATABASE CA 'Online!  CHEMICAL ABSTRACTS SERVICE, COLUMBUS,  OHIO, US;  TROYANOV, S. I. ET AL: "Packing in crystal  structures of metal.beta.-diketonates used  in MOCVD and its correlation to  volatility"  retrieved from STN  Database accession no. 128:264125  XP002219907  abstract  &amp; PROCEEDINGS - ELECTROCHEMICAL SOCIETY  (1997), 97-25(CHEMICAL VAPOR DEPOSITION),  886-892 ,</p> <p>---</p>	1-6,10, 13,15, 19,22, 31-40
X	<p>DATABASE CA 'Online!  CHEMICAL ABSTRACTS SERVICE, COLUMBUS,  OHIO, US;  LIM, JONG TAE ET AL: "Study on the  development of CVD precursors. II.  Synthesis and properties of new  lanthanum.beta.-diketonates"  retrieved from STN  Database accession no. 126:69303  XP002219908  abstract  &amp; BULLETIN OF THE KOREAN CHEMICAL SOCIETY  (1996), 17(11), 1023-1031 ,</p> <p>---</p>	1-6,10, 13,15, 19,22, 31-40
X	<p>WO 00 069863 A (RESEARCH FOUNDATION OF  STATE UNIVERSITY OF NEW YORK, USA)  23 November 2000 (2000-11-23)  the whole document</p> <p>---</p>	1-40
X	<p>US 6 099 903 A (KALOYEROS, ALAIN E. ET AL)  8 August 2000 (2000-08-08)  the whole document</p> <p>---</p> <p style="text-align: center;">-/--</p>	1-40

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 02/03657

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	<p>DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; WILLIAMS, PAUL A. ET AL: "The unusual thermal stabilization of MOCVD precursors by the dibenzoyl methanate group: liquid injection MOCVD of tantalum oxide and niobium oxide using M(OEt)4(dbm) precursors" retrieved from STN Database accession no. 137:145913 CA XP002219909 abstract &amp; CHEMICAL VAPOR DEPOSITION (2002), 8(3), 110-116 PUBLISHED IN: ADV. MATER. (WEINHEIM, GER.), 14(9) , 2002,</p> <p>-----</p>	1-40

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/GB 02/03657

### Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:  
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

### Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

#### Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

## FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

## Continuation of Box I.2

The initial phase of the search revealed a very large number of documents relevant to the issue of novelty. So many documents were retrieved that it is impossible to determine which parts of the claim(s) may be said to define subject-matter for which protection might legitimately be sought (Article 6 PCT). For these reasons, a meaningful search over the whole breadth of the claim(s) is impossible. Consequently, the search has been restricted to

1. The use of metal compounds with a general formula as given in claim 2, wherein M is Ti, Ta, Nb, or Pb;  $x > 0$ , R1 is phenyl, and R2 is methyl or phenyl;  $y > 0$ , D is an alkoxy group, in the field of MOCVD has been searched exhaustively.

2. Some documents relating to the use of the compounds of claim 1 in the field of MOCVD have been cited.

3. Some illustrative documents have been cited to illustrate the disclosure in the prior art of compounds with a general formula as given in claim 2, wherein M is Ti, Ta, Nb, or Pb;  $x > 0$ , R1 is phenyl, and R2 is methyl or phenyl;  $y > 0$ , D is an alkoxy group.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 02/03657

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 3153000	A	13-10-1964	NONE	
WO 8403042	A	16-08-1984	WO 8403042 A1 DK 481584 A FI 843745 A ,B, NO 844029 A	16-08-1984 08-10-1984 24-09-1984 08-10-1984
WO 00069863 3	A		NONE	
US 6099903	A	08-08-2000	AU 5143100 A WO 0070119 A1	05-12-2000 23-11-2000